Here we report *nonlinear* 1D layered materials that were fabricated by dispersing nonlinear dyes in alternate layers. These new materials have a modulation in the complex nonlinear refractive index in the direction normal to the surface of the layers. There are several potential applications of these nanostructured materials including optical limiting.

To obtain a broad bandwidth appropriate for the optical limiter applications, the layer thickness of the nanolayered samples can be varied or chirped. The thickness variation provides reflectivity over an appropriate band of wavelengths and acceptance angles. Such materials were fabricated using styrene-acrylonitrile (SAN) copolymers where the index difference between the layers was about 0.005. Figure 1 shows the spectrum of the reflected light from a 4096 layer sample with an average layer thickness of 87 nm compared to that of a sample with a 31 nm average layer thickness. The 87 nm layered film has a first order band gap in the visible whereas the band gap for the 31 nm film is at 197 nm, so the latter sample shows only the usual fresnel reflection. One of the SAN multilayered samples was cleaved perpendicular to the plane of the film. The thickness of the individual layers was then measured by atomic force microscopy (AFM). The layer thickness distribution derived from the AFM measurements is consistent with the width of the observed reflection spectrum in Figure 1.

Nonlinear nanolayered polymeric materials were fabricated by dissolving either lead tetrakis(cumylphenoxy)phthalocyanine ($PbPc(CP)_4$) or nigrosine into alternate layers of either SAN or polycarbonate structure. $PbPc(CP)_4$ is known to have a very strong nonlinear absorption and refraction coefficient.[2] The nigrosine has a broad absorption in the visible and an excited state that relaxes on the sub-picosecond time scale with the conversion of the absorbed energy into heat. The resulting rise in temperature causes a change in the refractive index. Nigrosine has been used in an effective refractive optical limiter.[3] The transmission as a function of incident fluence for a multilayer sample of a polycarbonate with nigrosine in alternate layers is shown in Figure 2. In these samples, the refractive index, n_0, of the dyed layers is initially larger than that of the undyed layer and the change in index with fluence of the nigrosine layers is negative. Hence the transmission is observed to increase with fluence as the layers approach index matching.

In summary, we demonstrated the fabrication of a variety of multilayer polymer films that exhibit a broadband reflectivity with index differences between the layers on the order of 0.005. We also demonstrated a fluence dependent transmission in a nonlinear nanolayered material.

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CMR2 **4:00 pm**

Diffractive lens fabrication by replica molding

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The fabrication of diffractive optical elements (DOE's) using a combination of electron-beam lithography and replica molding is detailed. Previous work has shown that diffractive optical lenses can be successfully fabricated with subwavelength features.[1–2] The challenge now is to fabricate a diversity of complex diffractive optical elements,[3] and to develop replica molding as a technique for their rapid and effective production.

Diffractive lenses and 2-D gratings were fabricated using electron-beam lithography and replica molding. With electron-beam lithography, feature sizes smaller than 60 nm can be achieved.[1] We demonstrate that we can achieve similar feature sizes with replica molding. High-fidelity replica molding can become an important tool to complement electron-beam lithography in the fabrication of DOE's and other nanostructures.[4–5]

Electron-beam lithography was used to fabricate the negative pattern in silicon. The electron-beam resist poly(methyl methacrylate) (PMMA) was spin-coated onto the substrate. Beam-writing was done with a Hitachi S-4500 SEM operating at a 30 kV acceleration voltage; the electron dosage was 160 μC/cm^2. Following exposure, the patterned PMMA was developed with 25% methylisobutyl ketone (MIBK) in isopropyl alcohol. A chemically assisted ion beam etch (CAIBE) was employed to etch the silicon layer using the remaining PMMA as a mask. The reactive gas XeF_2 was directed at the substrate with a flow rate of 30 sccm. High aspect ratios were achieved using this etch process—10:1 ratios of pillar height to width were fabricated with smooth side-walls. The 2-D gratings were etched to a depth of 530 nm, while the lens patterns were etched 600 nm deep.

Soft lithography was used to replicate the features of the lenses and gratings from silicon into silicone elastomer. Replica molding was done with polydimethylsiloxane (PDMS), which has been found to be a versatile material for soft lithography.[4–5] First the original silicon sample was coated with trimethylchlorosilane (TMCS), by exposing its surface to TMCS vapor. The mono-layer of TMCS acts as a non-stick coating; it prevents PDMS from adhering to the original sample's surface and both damaging the surface and impairing removal of the PDMS.[4]

The specific elastomer employed is GE silicone RTV 615A and 615B. Part "A" contains polydimethylsiloxane bearing vinyl groups and a platinum catalyst; part "B" contains a cross-linker containing silicon hydride (Si-H) groups. RTV is used in a 10 A : 1 B ratio for greatest mechanical strength.[4] RTV was mixed and spin-coated on the silicon samples to create a thin (~40 μm) layer; thin layers of RTV ensure high fidelity in replicating the sample's surface features. Following the spin-coat, the RTV was cured by baking at 80°C.

Diffractive lenses were fabricated using replica molding with subwavelength features intact, including 60 nm width rings. Ring height measured with an AFM matched the etch depth of 600 nm, and surface roughness was negligible (<5 nm). Thus, soft lithography techniques have potential as a method for fabricating optical nanostructures.

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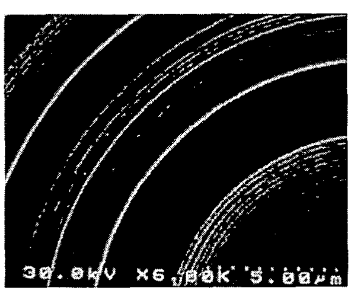

CMR2 Fig. 1 and 2. Diffractive lens patterned in silicon (left) and PDMS (right).

CMR3 **(Invited)** **4:15 pm**

Polymer Multilayer Optical Films: New Materials for Light Management

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Intro: Polymeric Optics

In this section the ever-expanding family of polymer-based optical films and devices will be placed into the context of the larger field of conventional, inorganic materials-based optical interference filters